THE INSTITUTE FOR MOLECULAR ENGINEERING

Simulations of Liquid Crystals

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Monte Carlo simulations of Liquid Crystals: A continuum approach

Liquid Crystal (LC) phases have been of great interest for scientist, mainly for their multiple applications in the develop of devices such as displays, due to a their extraordinary optical properties. However, in recent years, some researchers have found that LCs when confined on drops and when these interact with an external agent (e.g., biomolecules) it is possible to observe a phase transition[1,2]. The typical size of these systems are around 1 mm - 10 mm, so it is imperative to simulate these systems at a continuum level.

$$\mathbf{Q} = S\left[\mathbf{nn} - \frac{1}{3}\boldsymbol{\delta}\right]$$

Landau de Gennes

$$f_L = \frac{A}{2}\left(1 - \frac{U}{3}\right)\mathrm{tr}\left(\mathbf{Q}^2\right) - \frac{AU}{3}\mathrm{tr}\left(\mathbf{Q}^3\right) + \frac{AU}{4}\mathrm{tr}\left(\mathbf{Q}^2\right)^2.$$

Free energy functional using Q-tensor representation

$$F(\mathbf{Q}) = \int d^3\mathbf{x}\,[\underbrace{f_{LdG}(\mathbf{Q})}_{\text{Short range}} + \underbrace{f_E(\mathbf{Q})}_{\text{Long range}}] + \oint \underbrace{d^2\mathbf{x} f_S(\mathbf{Q})}_{\text{Surface}}$$

MC Metropolis: $\mathrm{P}^1_{\mathrm{acc}} = \min\left(1, \frac{\Delta F}{k_B T_i}\right)$

Elastic contribution

$$f_E = \frac{L_1}{2}\left(\frac{\partial Q_{ij}}{\partial x_k}\right)^2 + \underbrace{\frac{L_2}{2}\epsilon_{lij}Q_{lj}\frac{\partial Q_{ij}}{\partial x_k}}_{\text{Chiral term}}$$

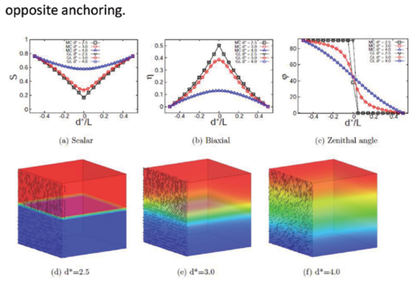
Surface contribution

$$f_{S,Surfactant} = \frac{1}{2}W\left(\mathbf{Q} - \mathbf{Q}^0\right)^2$$

$$f_{S,Water} = \frac{1}{2}W\left(\hat{\mathbf{Q}} - \hat{\mathbf{Q}}^\perp\right)^2$$

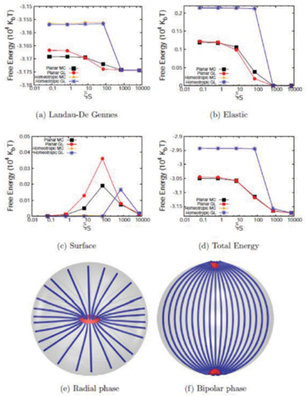
Hybrid Cell

In order to verify our MC method, we studied the so-called hybrid cell, where the LC is confined between plates with opposite anchoring.



LC Droplet

Also, LC droplets were studied using the new MC approach by doing a comparison with results obtained from GL relaxation.

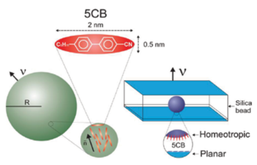


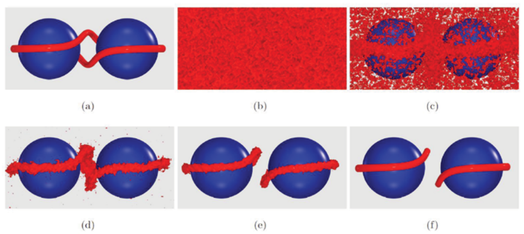
Above is a comparison of free-energy contributions as a function of surface interaction. In many cases, both GL and CM predict similar droplet morphologies; however, in some cases, each predicts different equilibrium.

Meta-Stable States within a Channel

A popular area of investigation is the behavior of multiple micrometer-sized particles within an LC cell. These previous studies include theoretical, computational and empirical work.

Particles with perpendicular anchoring, when placed in an LC channel, possess Saturn-ring defects. These defects can interact, encouraging locally stable states. Shown right is one example of this: (*a*) A locally stable, twisted-defect configuration; (*b-d*) With increasing temperature, the LC becomes isotropic, destroying the defect; (*e,f*) Upon cooling, a more stable defect structure is found.





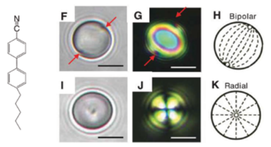
Reference

[1] I.-H. Lin, D. S. Miller, P. J. Bertics, C. J. Murphy, J. J. de Pablo and N. Abbott, Science, 2011, 332, 1297.

[2] J. A. Moreno-Razo, J. P. Hernandez-Ortiz, E. J. Sambriski, N. L. Abbott and J. J. de Pablo, Nature, 2012, 485, 86

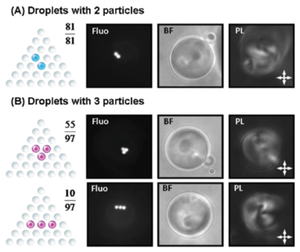
Nanoparticle Interactions on an LC Droplet

This section will discuss our work on nanoparticles placed at the interface of a liquid crystal (LC) droplet. These micrometer-sized LC droplets are the result of mixing water with a liquid crystal such as 5CB. Previously, bare droplets have proven effective as bio-sensors, undergoing phase transitions when minute concentrations of specific biomolecules are present.



First, diagram of 5CB molecule, very common LC. Next three, micrographs and sketch showing internal structure of two different droplet phases. The dashed lines denote molecular orientation. (Abbott Lab)

Because this is a relatively large system, a continuum approach is employed. Both the average molecular direction and degree of alignment is contained in the alignment tensor. With the given expression for the free energy and a numerical algorithm to minimize it, we can calculate equilibrium properties.



Arrangement and relative frequency of two- and three-particle systems (*left*). Corresponding micrographs on right.

$$F[\mathbf{Q}, \nabla\mathbf{Q}] = \int f_B(\mathbf{Q}, \nabla\mathbf{Q})\; d^3\mathbf{x} + \int f_S(\mathbf{Q})\; d^2\mathbf{x}$$

$$\Pi\left(\frac{\delta f_{surf}}{\delta \nabla\mathbf{Q}} \cdot \boldsymbol{\nu} + \frac{\delta f_{bulk}}{\delta \mathbf{Q}}\right) = 0$$

$$\Pi\left(\frac{\delta f_{bulk}}{\delta \mathbf{Q}}\right) = 0$$

$$Q^{t+\Delta t}_{bulk,ij} = Q^t_{ij} - \frac{\Delta t}{\Gamma} h^{bulk}_{ij},$$

$$Q^{t+\Delta t}_{surf,ij} = Q^t_{ij} - \frac{\Delta t}{\Gamma} h^{surf}_{ij}$$

Schematic for LC droplet with particles. Blue interior is the simulated region. The black outline and circles represent the LC-droplet interface and nanoparticles, respectively.

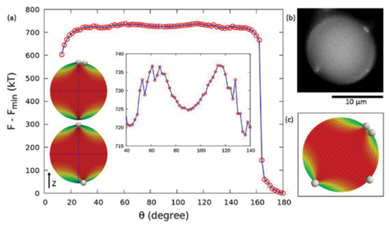
Our wish was to better understand and clarify the results shown to the left. For example, what is the orientation of the droplet field in relation to the particle arrangement? And, equally important, what is the molecular structure surrounding each particle?

Here, our multi-particle results will be discusses. For all of the numerical results presented, experimental findings are also given. In all cases, there is excellent agreement between the two approaches.

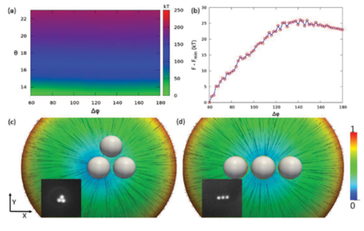
Simulation and Experiment

Shown here are numerical results for a three-particle system. Right is a plot of free energy as a function of angle. The two images on the right are a direct comparison between our prediction and experiment.

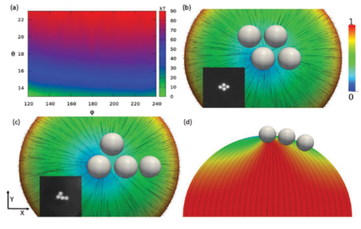
This plot has two minima: a global minimum when two particles are touching at one pole and the third particle is antipodal to the first two; and a second, less obvious minimum around 90 degrees. Both of these minima have been found as stable states in experiment; the upper-right micrograph confirms this.



Four-particle clusters – With increasing particle number, more particle arrangements become possible. As with two- and three-particle systems, our numerical results agree with experiment. For each configuration, experimental results are shown in the bottom left.



Three-particle clusters – In additoin to remaining in a line, three particles can also form a cluster. Shown below are minimum-energy states for a three-particle cluster. Experimental results also shown.

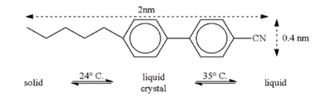


Relevant Work:
NL Abbott at UW Madison; S Zumer at University of Ljubljana; OD Lavrentovich at Kent State University

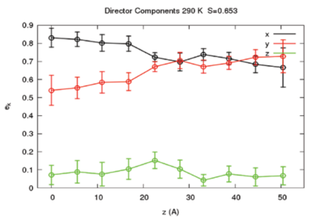
Molecular Dynamics simulation of Lipid A at 5CB-Water Interface

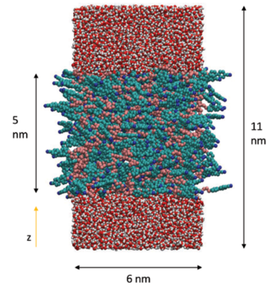
Many properties of liquid crystals (LCs), such as the phase transition temperature, the stability of particular phases, and its diffusion properties, are very sensitive with respect to molecular structure. Molecular dynamics (MD) simulation is able to examine the role of molecular structure and charge distribution in determining phase behavior. We have employed MD to study the ordering of 5CB molecules at a water interface and the effect of the presence of lipid A at this interface on the local ordering of the 5CB molecules.

For simulation of 5CB, we have used the force field developed by Zhang, et al. [1]. This model has a nematic-isotropic temperature transition around 308K.



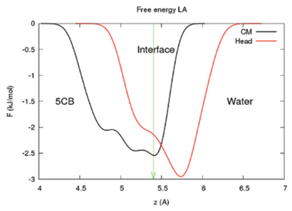
Simulation of 5CB-water

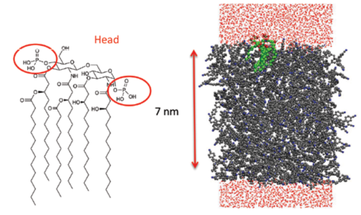




The director of the 5CB molecules changes with distance from water interface. 5CB molecules tend to be oriented parallel (planar) to the water surface.

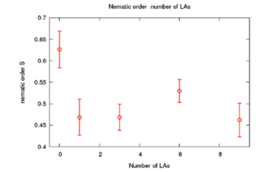
Simulation of lipid A at the 5CB-water interface





Our Calculations of free energy suggest that the head of lipid A is more likely to be located in the water while the total center of mass is close to the interface. This proves that the tails of lipid A is immersed in 5CB. As it was observed in experiment, immersing the tails in the 5CB can modify the orientation of 5CB from planar to homotropic [2]. Therefore the effect of the presence of lipid A at 5CB-water interface on the local ordering of the 5CB molecules is qualitatively studied by adding lipid A molecules.

Adding lipid A to the 5CB-water modified the nematic degree of alignment. Our results show that lipid A can change the LC phase from nematic (planar) to disordered.



References:

[1] Zhang, J., Su, J., & Guo, H. (2011). An atomistic simulation for 4-cyano-4'-pentylbiphenyl and its homologue with a reoptimized force field. *The Journal of Physical Chemistry. B*, *115*(10), 2214–27. doi:10.1021/jp111408n

[2] Lin, I.-H., Miller, D. S., Bertics, P. J., Murphy, C. J., de Pablo, J. J., & Abbott, N. L. (2011). Endotoxin-induced structural transformations in liquid crystalline droplets. *Science (New York, N.Y.)*, *332*(6035), 1297–300. doi:10.1126/science.1195639

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